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DETERMINATION OF AROMATICS IN HYDROCARBON MIXTURES

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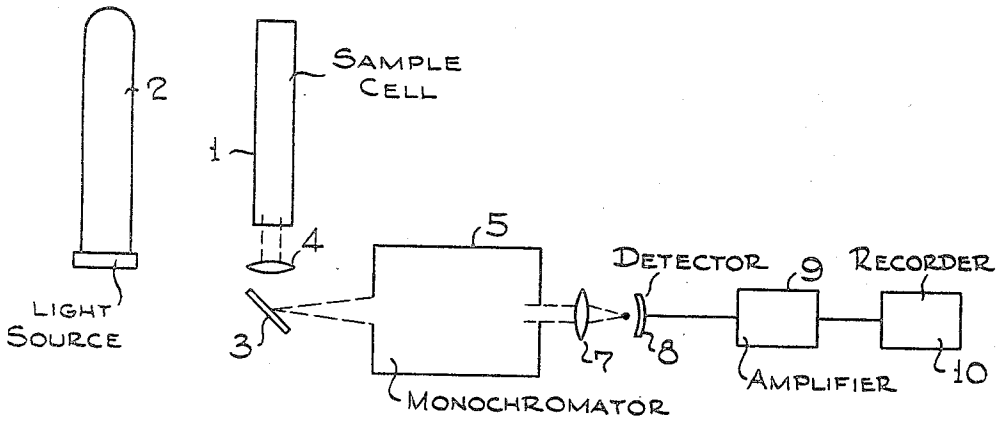
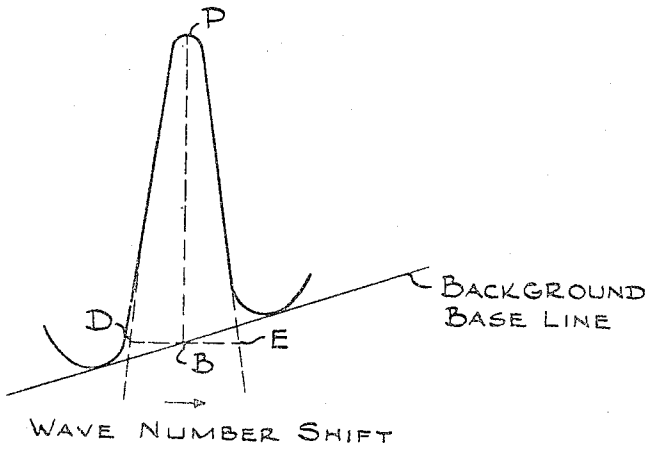


FIG.-1

FIG.-2



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DETERMINATION OF AROMATICS IN HYDROCARBON MIXTURES

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1 Claim. (Cl. 88—14)

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This invention relates to an improved method for determining the precentages of aromatics in hydrocarbon mixtures. In accordance with this invention, a suitable light source and associated apparatus are employed in conjunction with a sample of a hydrocarbon mixture to be analyzed so that Raman lines are produced. The Raman lines characteristic of the particular hydrocarbon mixture are then analyzed according to the process of this invention to enable the determination of the total aromatic content of the hydrocarbon mixture.

In the chemical industry generally, and particularly in the petroleum refining industries, it is frequently of importance to be able to determine the percentage of aromatics present in a hydrocarbon mixture. Such determinations may be made for a wide variety of purposes. For example, it may be useful in adjusting fuel quality to determine the aromatic content of a base fuel stock. Again it may be desired to add particular percentages of aromatics to a base fuel stock, the aromatics being added in the form of a hydrocarbon mixture of uncertain or varying composition. The present invention is therefore of application in any situation wherein it is desired to establish the aromatic content of a hydrocarbon mixture.

As is well-known, when a beam of light is passed through certain substances, part of the light is scattered so as to produce light of a wave length different from that of the exciting radiation. This scattered light constitutes the Raman spectrum of the particular substance. If the Raman spectrum is examined, it is found that it consists of a series of lines of extremely low intensity having both longer and shorter wave lengths than the exciting line. A basic principle on which this invention depends is the discovery that certain Raman lines are always produced when aromatics are subjected to exciting light. Thus, when a hydrocarbon mixture containing aromatics is subjected to an exciting light, it will be found that Raman lines will be produced uniquely characteristic of the aromatics present, even though many other Raman lines are produced by other constituents of the hydrocarbon mixture. It has furthermore been discovered that a definite relation exists between the intensity of the Raman line and the concentration of the aromatics present. Consequently, in light of these basic principles, the process of this invention has been developed, making possible the identification of the percentage of aromatics present in a mixture from a consideration of the Raman spectrum produced from the mixture.

In order to permit a thorough understanding

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of this invention, the following description has been prepared directed to an explanation of the accompanying drawings wherein:

Figure 1 diagrammatically represents a suitable type of apparatus which may be utilized in obtaining the Raman spectrum of a particular mixture; and

Figure 2 represents a typical record resulting from the scanning of a portion of the Raman spectrum showing the derivations of the quantities "scattering coefficient" and "peak base width" used in the analysis procedure of this invention.

Referring now to Figure 1, the numeral 1 designates a sample cell in which the hydrocarbon mixture to be analyzed may be held. The sample cell may conveniently be constructed of glass. Suitable openings are provided in the cell to permit introduction of the hydrocarbon mixture to be analyzed, which may be either a liquid or a gas. It is to be noted, however, that the present invention is of greatest utility in determining the percentages of fairly high boiling aromatics so that in general the mixture to be analyzed will consist of a liquid mixture of hydrocarbons. Due to the light to which the sample cell is exposed, the sample cell may become quite hot; consequently, it is generally the practice to surround the sample cell except for the faces thereof with a suitable cooling jacket so as to permit maintaining the cell at a reasonable temperature. It is furthermore the general practice to suitably shield the sample cell with a medium adapted to absorb undesired light energy.

A suitable light source 2 is positioned adjacent the sample cell 1 in such a manner as to cause light to fall on the cell. If desired, a second light source may be positioned on the opposite side of sample cell 1 so the light may be thrown on the cell from both sides thereof. It is desirable that the light source 2 be of such a character as to provide predominantly light energy of a single frequency. For example, it is suitable to employ a mercury vapor lamp or a sodium vapor lamp as the light source 2. It is clearly important to use a light source having as great an intensity of light as is practical. In accordance with the principles discovered by Raman, when light from the source 2 falls upon the mixture of hydrocarbons in cell 1, scattered light will be produced which may be readily detected at a point outside the general path of light from the source 2. For example, scattered light or Raman lines will be produced from the mixture in cell 1 which may be detected at the position occupied by the mirror 3 in Figure 1. Thus, the Raman lines produced from the hydrocarbon

mixture may be focused by a suitable lens system 4 so as to fall on the mirror 3. The Raman lines are reflected from the mirror 3 into the entrance slit of a monochromator 5. The total Raman lines introduced to the monochromator 5 are dispersed by the monochromator into a Raman spectrum which may be observed at the focal plane of the exit slit of the monochromator. In the actual practice of this invention, a drive assembly is employed in conjunction with the monochromator so that the lines of the Raman spectrum are continuously scanned across the exit slit of the monochromator. Adjacent the exit slit and in the path of the light emitted therefrom, is positioned a suitable lens system 7 to cause the light issuing from the monochromator to fall on a suitable detector 8. While sensitized photographic plates, or other detecting means may be employed, it is a particular feature of this invention that a photo multiplier tube be used as the detector element. The output of the photo multiplier tube may then be amplified by a suitable amplifier 9 and this amplified output may be recorded by a high speed recorder 10. The record of the recorder 10 will consist of a continuous plot of wave length vs. intensity over the wave lengths for which the monochromator is adjusted to scan.

In considering the nature of the light energy detected by the detector 8, it will be found that a high intensity signal will be received at a wave length corresponding to that of the light source used and that lower intensity signals will be received at higher and lower wave lengths. Thus in the case in which the light source 2 is a mercury vapor light source, the detector 8 will register a high output for 4,358 angstrom units. Longer and shorter wave length light of markedly lower intensity will also be received, falling on either side of the wave length of the exciting light. In general, the lines falling on the longer wave length side of the exciting light are conveniently employed in the practice of this invention. A suitable method of expressing the nature of the lines is to express their spectral position in terms of their distance from the exciting line expressed in wave numbers. This frequency difference may be designated as the "wave number shift" ($\Delta \bar{\nu}$ cm.$^{-1}$).

If a continuous Raman spectrum, such as that emitted from a hydrocarbon mixture excited by suitable light, is examined, it will be found that above the wave length of the exciting light, the intensity of the light will vary as a function of the wave length in a manner which may be represented on a curve by peaks and valleys. This is true since all hydrocarbons have characteristic Raman spectra so that the presence of particular hydrocarbons will cause an increase in the intensity of the Raman spectra at particular frequencies. In the case of aromatic type hydrocarbons it has been found that Raman lines are obtained which are concentrated in the 1590 to 1615 wave number shift region. This effect provides a convenient manner for determining the total aromatic content of a hydrocarbon mixture. In actual practice, however, a complication which arises is that in continuously scanning a spectrum emitted by a hydrocarbon mixture, slight shifts in the intensity at the point at which the characteristic aromatic lines appear will be encountered. This is principally due to slight fluctuations in the intensity of the light source and to variations in the output of the detector and electronic components associated therewith. To correct for this effect, it is generally the practice to utilize a suitable control standard such as carbon tetrachloride. While carbon tetrachloride will be used as an example of a suitable control standard throughout this specification, many other control standards may be employed. Thus the standard chosen may be one which is available in pure form and having distinct Raman line, preferably of about the same intensity as the lines of the sample. Alternatively the control sample may constitute a synthetic blend of known composition; for example, having a known composition similar to that of the sample being analyzed. In order to use the control sample, such as carbon tetrachloride, it is necessary to periodically remove the sample cell containing the hydrocarbon mixture to be analyzed, and to replace the sample cell with a sample cell containing carbon tetrachloride. It is convenient to use the Raman line of the carbon tetrachloride occurring at a wave number shift of 459 ($\Delta \bar{\nu}$ cm.$^{-1}$). In order to suitably correct variations of intensity of the Raman lines of the hydrocarbon mixture, an expression called the "scattering coefficient" is evaluated. The scattering coefficient my be defined as the ratio of the intensity of the particular line concerned to the intensity of the chosen line of the control sample. In order to evaluate this formula, it is convenient to measure the height of the lines on the record chart produced by the recorder 10 of Figure 1, measured in millimeters above the background base line.

Figure 2 diagrammatically indicates the type of intensity variation recorded by the recorder 10 as a portion of the Raman spectrum is scanned. It will be noted that a peak intensity is indicated at a point identified as "P" on the curve. On either side of the peak intensity, the intensity of the signal recorded drops off sharply to a value indicated as being the "background base line." If lines are drawn along the sharply sloped portions of the curve on either side of point P, as indicated, a more or less triangular area will be obtained having the base D—E and bounded by the indicated construction lines and by the sharply peaked curve. On the plot of Figure 2 the scattering coefficient may then be defined to be the distance PB of the particular intensity peak examined, divided by the similar distance PB derived from the height of the carbon tetrachloride peak. It is apparent that the area below the curve of Figure 2, may be approximately determined by finding the area of the triange indicated, having the vertices P, D, and E. This area is defined as the scattering area and is equal to the scattering coefficient times the base width divided by two.

As stated, a characteristic Raman line intensity peak will be found for aromatics in the 1590 to 1615 wave number shift region. However, a particular aromatic compound will produce a Raman line within this region having a somewhat different wave number shift than that of a different aromatic compound. Consequently, in order to eliminate the effect of this variation in the point at which characteristic lines appear for different aromatic compounds, it is desirable to utilize the total area under the curve of the Raman spectrum in the indicated wave number shift region.

With the foregoing brief description of the general principles and techniques involved in the method of this invention, the manner in which the percentage of aromatics present in a sample may be determined may be readily understood.

Indicated in Table I are the results obtained in analyzing 22 pure aromatic hydrocarbons by the technique of this invention.

TABLE I

Raman spectral data in the 1,590 to 1,615 cm.$^{-1}$ region for pure aromatic hydrocarbons

Aromatic Hydrocarbon	Wave No. Shift	Scattering Coefficient	Peak Base Width (mm.)
Benzene	1,590	0.291	17.3
Toluene	1,600	0.297	17.0
Ethylbenzene	1,600	0.288	15.0
Meta-xylene	1,595	0.187	16.2
Para-xylene	1,615	0.315	10.5
Ortho-xylene	1,600	0.235	17.0
Isopropylbenzene	1,605	0.248	15.8
Normal propylbenzene	1,600	0.249	16.0
Meta-ethyltoluene	1,610	0.198	15.8
Para-ethyltoluene	1,605	0.279	13.0
1,3,5-Trimethylbenzene	1,600	0.223	16.8
Ortho-ethyltoluene	1,595	0.239	17.6
1,2,4-Trimethylbenzene	1,615	0.261	11.2
1,2,3-Trimethylbenzene	1,590	0.215	13.8
Hydrindene	1,600	0.217	15.5
Tertiary butyl benzene	1,595	0.227	16.0
Isobutylbenzene	1,600	0.235	15.5
Secondary butyl benzene	1,600	0.244	16.0
Meta-cymene	1,600	0.203	15.5
Para-cymene	1,615	0.370	13.2
Ortho-cymene	1,605	0.223	17.7
Normal butylbenzene	1,590	0.228	14.5
Average		0.249±0.031	15.3±1.5
Deviation from average, per cent		12.4	9.8

It will be noted that for each compound the Raman shift observed is given, the scattering coefficient is given, and the peak base width is stated. The significance of each of these quantities is as formerly defined. As shown by the table, the scattering coefficients for each of the aromatic hydrocarbons is substantially constant. Thus, the average scattering coefficient is 0.249 and this value is correct for any of the aromatic hydrocarbons plus or minus 0.031. Similarly, the base width for each of the aromatics is substantially the same, having a value of 15.3 plus or minus 1.5. In order to determine the percent of total aromatics in a sample, therefore, it follows that the percent by volume of aromatics is equal to the observed scattering coefficient times the observed base width measured in millimeters divided by the product of 0.249 (average scattering coefficient from pure compound data) and 15.3 (average base width from pure compound data in millimeters) all multiplied by 100. This formula is indicated below.

$$\text{Percent aromatics} = \frac{\text{Scattering coefficient} \times \text{peak base width}}{(0{,}249)(15.3)} \times 100$$

Consequently, in order to determine the percent by volume of aromatics present in a sample, it is only necessary to determine the scattering coefficient of the sample in the 1590–1615 cm.$^{-1}$ region and to determine the base width of the aromatic peak in millimeters.

Indicated in Table II are the analytical results obtained by applying this method to the analysis of synthetic blends in order to determine the total aromatics.

TABLE II

Raman analyses of synthetic blends for total aromatics

Blend No.	Components Present	Aromatics (Per Cent by Volume)		Deviation from Reported Value (Per Cent)
		PerCent	Found	
1	Xylenes	96	95	1.0
2	Xylenes+40% 2,2,4-trimethylpentane	57.5	53	7.8
3	Solvesso 100 [1]	95	93	2.1
4	Solvesso 100+40% 2,2,4-trimethylpentane	56	54	3.6
5	Solvesso 100+80% 2,2,4-trimethylpentane	18.6	16.5	11.3
6	Solvesso 100+92% 2,2,4-trimethylpentane	7.4	7.5	1.0
7	Solvesso 100+20% 2,2,4-trimethylpentane+40% trans-heptene-3	37	33.5	9.5
	Average deviation			5.3

[1] Solvesso 100 is a commercial solvent naphtha boiling between 300 and 365° F.

It will be noted that 7 sample blends were employed, having the characteristics noted in the table. In each case, the analytical procedure was successful in establishing the total aromatic content of the samples with an average per cent deviation of 5.3.

As a further example of the application of this invention, analyses were made of an aromatic concentrate consisting of the 312.7 to 338.8° F. fraction from a 40 plate fractionating column used in fractionating a catalytically cracked naphtha. This fraction of the catalytically cracked naphtha was subjected to conventional Raman spectographic analysis procedures and to the analysis procedure of this invention to determine the percentage of constituents in the sample. To accomplish this, the sample was distilled in several fractions to yield fractions which could readily be analyzed by the conventional Raman spectrographic procedure. These fractions are identified in the accompanying Table III as the "distillation fractions."

TABLE III

Raman analysis of an aromatic concentrate

Distillation Fractions	1	2	3–12	13–21	22–28	29–33	34–R12	Bottoms	Summation of Blend Analyses	Total Sample Analysis
Constituents										
Ortho-xylene	3								0.1	
Isopropylbenzene										
Normal propylbenzene	13	8.5	0						0.5	
Meta-ethyltoluene	20	39	50	5					15.1	16.8
Para-ethyltoluene	7	8	20	21.5					10.3	10.9
1,3,5-Trimethylbenzene			0	31	60	20	0		20.0	16.8
Ortho-ethyltoluene				8.5	28	12.5	0		8.4	6.2
1,2,4-Trimethylbenzene						23	60	76	14.4	14.5
Summation for conventional analysis	43	55.5	70	66	88	55.5	60	76	68.8	65.2
Total aromatics (from 1,600 cm.$^{-1}$ Raman line)	44	60	76	71	85	50	65	81	69.8	70.0
Deviation, per cent	2.3	8.2	8.6	7.6	3.4	9.9	8.3	6.6	1.5	7.4

As indicated by the summation column given in the table, fraction 1 by conventional methods was found to have 43% total aromatics. Applying the method of this invention, it was found that the total aromatic content was 44% indicating a deviation of 2.3%. Similarly, each of the other fractions were analyzed by conventional methods to give the results indicated in the table, which results were compared to the results obtained by applying the method of this invention. It will be noted that the percentage deviation for each of the separate fractions varied from 2.3% to 9.9%. As a check against this procedure, the last vertical column of the table indicates a summation of the analyses of the separate fractions. It will be noted that using the conventional analysis procedures, a value of 68.8% aromatics was obtained. The per cent aromatics as determined by the method of this invention was found to be 69.8% representing a percentage deviation of 1.5%.

It will be apparent to those skilled in the art that the broad method of this invention may be refined and modified in many ways. For example, electrical computing devices and various charts may be employed to facilitate the analytical determinations. Again it may be desirable to utilize a Raman spectrograph which is provided with slits of a suitable width to just cover the 1590 to 1615 wave displacement region of the spectrum.

What is claimed is:

The method of quantitatively determining the total aromatic hydrocarbon content of a liquid sample consisting of the steps of scanning the Raman spectrum of the said sample in the 1590 to 1615 wave number displacement region, producing a curve expressing the variation of intensity within this region, and measuring the peak intensity and the peak base width of the curve of intensity within this region above the base background intensity whereby the total area beneath the intensity curve above the background intensity within this region may be determined and whereby the total aromatic content of the sample may be obtained.

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